Refractory Boron Compounds for High Performance: Theory and Experiment

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Abstract: We have shown that novel synthesis methods combined with careful evaluation of DFT phonon calculations provides new insight into boron compounds including a capacity to predict T_c for AlB_2-type superconductors.

Introduction: Our interest focuses on the refractory, or ceramic, forms of boron as they show performance parameters that are critical for future technological applications. For example, use of metal diborides as superconductors, metal hexaborides as metallic conductors and as semiconductors and their use under extreme conditions are key drivers of this work.

Multiple use of these refractory compounds is due in large part to boron's versatile bonding capacity. Boron itself can form as covalently bonded molecular networks while many boron compounds are electron deficient. Hexaborides show ambiguous bonding character; for example, covalent, metallic and ionic bonding can co-exist [1] in LaB_6. Within a specific structure type, substitution of the metal atom with a different metal of similar charge (e.g. replace La with Y in MgB_6) or co-substitution (e.g. $Mg_{1-x}Al_xB_2$) can significantly influence electronic properties that range from metallic conductor to superconductor or insulator to superconductor. The use of metal substitution in a high symmetry structure without abrupt changes in phase or crystallography enables the design, using Density Functional Theory (DFT), of new boron compounds with targeted, or predictable, electronic properties. Once determined, or designed, the challenge is then to synthesise a new compound.

Many methods have been employed to synthesize diborides and hexaborides albeit for MgB_2 current commercial methods exploit powder-in-sealed-tube (PIST) techniques [2]. This approach utilises steel tubes to encapsulate elemental boron and magnesium which are then subjected to temperatures >800^{o}C to effect formation of the required product. We have explored synthesis of MgB_2 within steel reactors at lower temperatures using intermediate borohydride compounds [3]. The choice of new boron compositions for synthesis is informed by Density Functional Theory (DFT) calculations which, with careful analysis, we show are reliable predictors of superconductivity [4]. Phonon dispersions are key indicators of performance for diboride [4, 5] and other boride structures.

Methods: We have exploited vapour deposition methods using a 50mL Inconel 601 Parr reactor with a significant temperature gradient (~250^{o}C–300^{o}C) from the base to the top of the reactor. The reactor is operated within a controlled atmosphere glove box containing Argon (99.99%). We use Materials Studio V7.0/8.0 for DFT modelling using CASTEP [6]. A linear response within the local density approximation (LDA) and generalized gradient approximation (GGA) with a dense k-grid mesh (i.e. < 0.03 A^{-1}) is applied to all structural variants [5].

Results: Synthesis methods allow control of particle size, morphology, crystallinity and phase abundance in the final product. High quality, micron-sized interpenetrating grains of MgB_2 are produced at low temperatures (~500–600°C) under autogenous pressure by pre-mixing Mg powder and $NaBH_4$ and heating in the reactor for 5–15 h [3]. Variation of the heating profile (Fig 1.) within this reactor shows that MgB_2 forms over a range of autogenous pressures (1–2 MPa) but with highly variable quality and quantity of

product(s). This variability of output is due to the relative influence of at least three key equilibrium reactions at 75ºC–120ºC, 200ºC–300ºC and 450ºC–550ºC. Raman spectroscopy and electron microprobe analyses provide strong evidence that surface decomposition of MgB_2 can be rapid under standard laboratory conditions.

DFT calculations for both diboride and hexaboride superconductors (e.g. MgB_2 and YB_6) reveal a strong link between components of phonon dispersion (PD) plots and the form of the Fermi surface. We have linked these components, which include the Kohn anomaly, to specific electronic properties [4]. For example, in both diborides and hexaborides, the absence of a Kohn anomaly in well-constructed PD calculations, implies limited or no capacity for superconductivity. However, the depth (or intensity) of the anomaly (e.g. Fig. 2) is a compelling indicator of superconductivity and the transition temperature [4]. This approach provides an essential tool for deliberate targeting of structures (e.g. AlB_2-type) and compositions (e.g. borides) with T_c values higher than currently achieved for MgB_2. For example, we propose that substituted variants of MgB_2 such as $Mg_{1-x}Ba_xB_2$, will show $T_c > 60$ K when successfully synthesised [4]. Further, the approach is applicable to other superconducting structures with strong electron-phonon coupling.

Conclusions: Systematic evaluation of structure-dependent electron-phonon parameters using DFT modelling aligned with novel synthesis conditions provides an opportunity to design and develop new high performance materials for electronics, photovoltaics and energy applications.

References:

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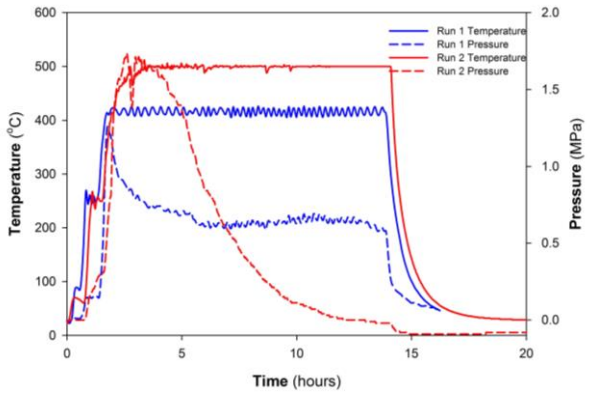

Fig. 1. Temperature – pressure reaction conditions for MgB_2 [3].

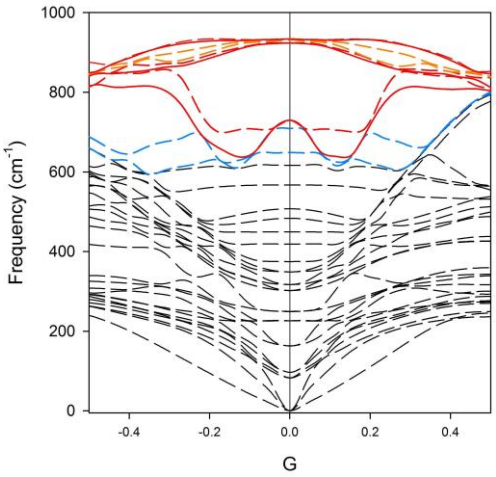

Fig. 2. PD for $Mg_2Al_2B_8$ showing phonon anomaly.